

Earth and Planetary Materials

Spring 2013

Lecture 9
2013.02.06

Work sheet from last lecture

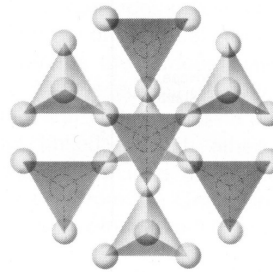
1. Name the main types of silicate minerals with schematic drawings of their main structural components.
2. Define miscibility gap and give an example.
3. List the similarities and differences of pyroxenes and amphiboles.
4. What is the difference between the dioctahedral and trioctahedral sheet silicates? Give examples for each.
5. What is the difference between antigorite and chrysotile?
6. And...what is the difference between chain silicate TOT and sheet silicate TOT?

Tectosilicates (framework silicates)

Silica minerals
Feldspar minerals
Feldspathoids
Zeolites

Tectosilicates

- ~64% of Earth's crust
- Contain networks of SiO_4 tetrahedra that share all four oxygens with other tetrahedra
- Stable, strongly bonded structure with $\text{Si}:\text{O} = 1:2$
- Main types:
 - Silica minerals
 - Feldspars
 - Feldspathoids
 - Zeolites



All oxygens are bridging oxygens

Silica minerals – SiO₂

Nine polymorphs

- Stishovite (rutile structure, Si in octahedral coordination)

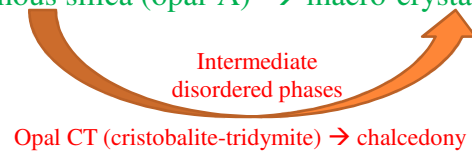
Name	Symmetry	Space Group	Specific Gravity	Refractive Index (Mean)
Stishovite*	Tetragonal	<i>P4₂/mnm</i>	4.35	1.81
Coesite	Monoclinic	<i>C2/c</i>	3.01	1.59
Low (α) quartz	Hexagonal	<i>P3₂21</i> (or <i>P3₁21</i>)	2.65	1.55
High (β) quartz	Hexagonal	<i>P6₂22</i> (or <i>P6₁22</i>)	2.53	1.54
Keatite (synth.)	Tetragonal	<i>P4₁2,2</i> (or <i>P4₃2,2</i>)	2.50	1.52
Low (α) tridymite	Monoclinic or Orthorhombic	<i>C2/c</i> (or <i>Cc</i>)	2.26	1.47
High (β) tridymite	Hexagonal	<i>P6₃/mmc</i>	2.22	1.47
Low (α) cristobalite	Tetragonal	<i>P4₁2,2</i> (or <i>P4₃2,2</i>)	2.32	1.48
High (β) cristobalite	Isometric	<i>Fd3m</i>	2.20	1.48

*Only polymorph with Si in octahedral coordination with oxygen.

Related phases (non- bulk-crystalline)

- Chert (micro-crystalline quartz), flint, opal (SiO₂·H₂O, locally ordered structure of silica spheres and highly variable H₂O content)
- In sedimentary basins @ low T

amorphous silica (opal-A) → macro-crystalline low (α) quartz

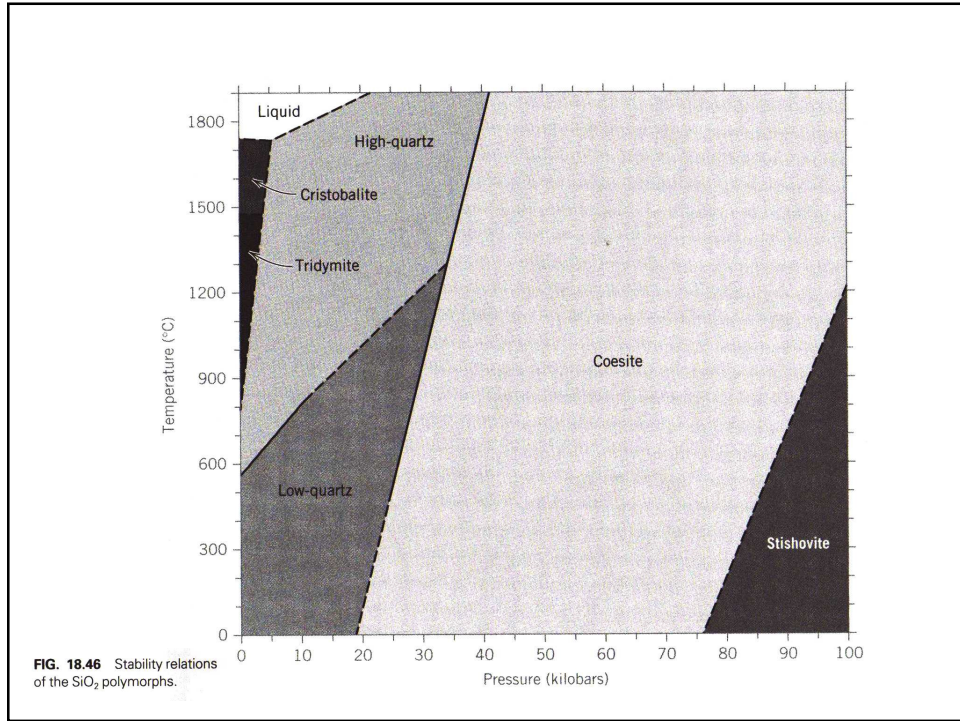


Stability of polymorphs is dependent on lattice energy

- High T phases: great lattice energy, more expanded structures, lower specific gravity

Three principal, naturally occurring polymorphs

- *Low quartz*: lowest symmetry, most compact structure
- *Low tridymite*: higher symmetry, more open structure
- *Low cristobalite*: highest symmetry, most expanded structure of the three



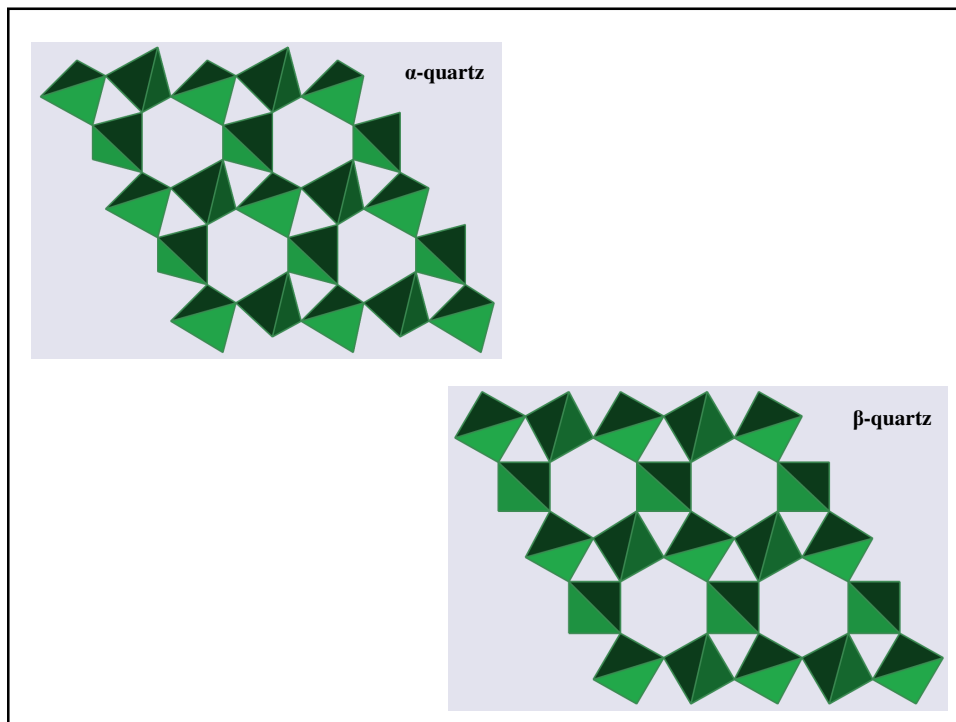
Two types of transition between silica minerals

1. **Displacive** – no bond breaking, involves tilting of tetrahedra (bond bending)

- Requires very little energy
- Rapid
- Reversible
- Phases related by displacive transition usually don't occur inside the stability field of the other phase

Examples:

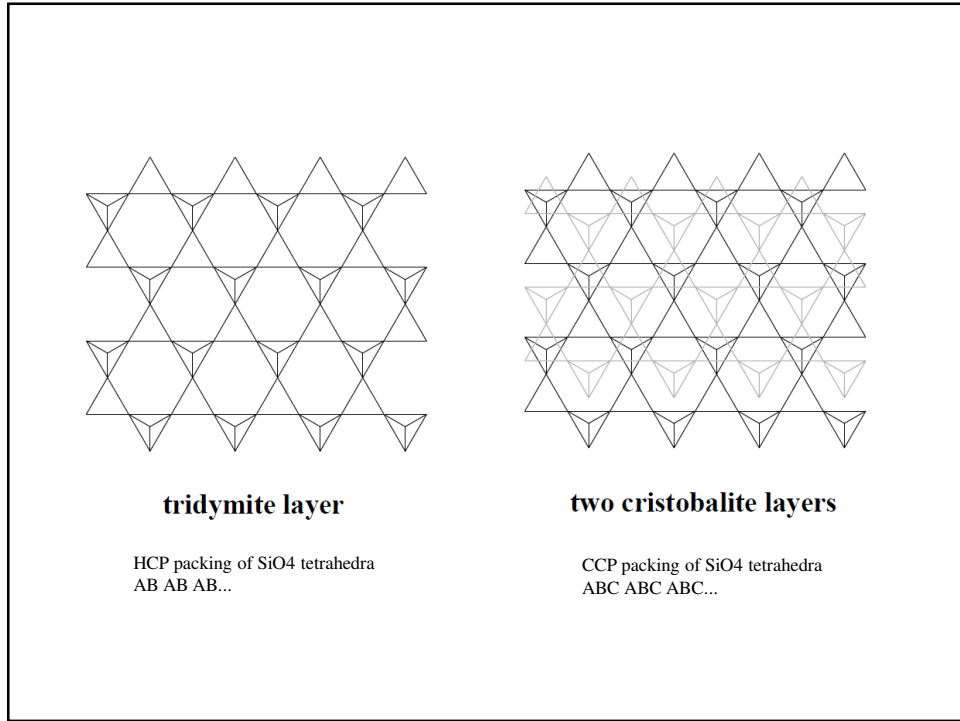
- Low quartz → high quartz
- Low tridymite → high tridymite
- Low cristobalite → high cristobalite



2. **Reconstructive** – requires bond breaking, re-arrangement of atoms

- Requires a lot of energy
- Slow, sluggish
- Common to find mineral outside its stability field (where it is metastable)

Examples: most of the transitions between silica minerals
quartz – tridymite – cristobalite



Quartz

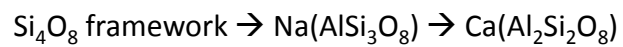
- Common in sedimentary, metamorphic, igneous rocks
- Transparent in both IR and UV light regions
 - Applications: optical lenses, prisms
- Piezoelectricity (physical property)
 - Develops an electrical potential when deformed
 - Deforms when subjected to an electric field
 - Applications: quartz oscillators, quartz watches, etc

Feldspar minerals

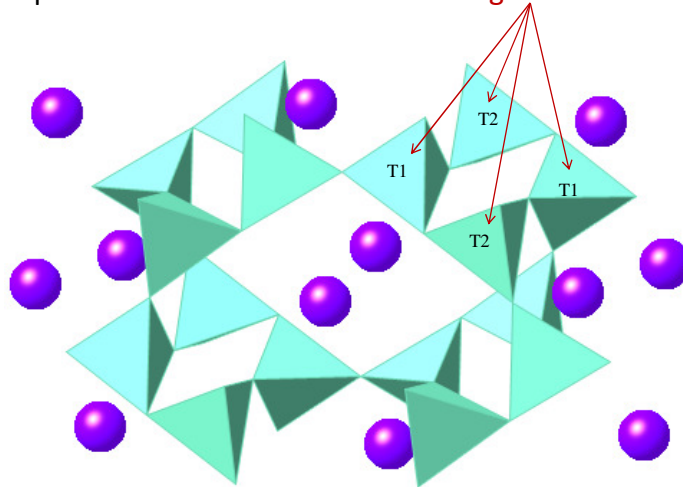
- Most abundant mineral group in Earth's crust
- Produced when Al^{3+} substitutes for Si^{4+} in the framework structure
 - coupled substitution with large cations (+1 or +2)

Structure

- "stuffed" derivative of SiO_2 structure (Al → Si, fill cations at voids)



- Composed of chains of 4-membered rings of tetrahedra



Structure of sanidine
(high-temperature polymorph of KAlSi_3O_8)

- Chains are crankshaft-like, cross-linked, and form voids filled by K, Na, or Ca

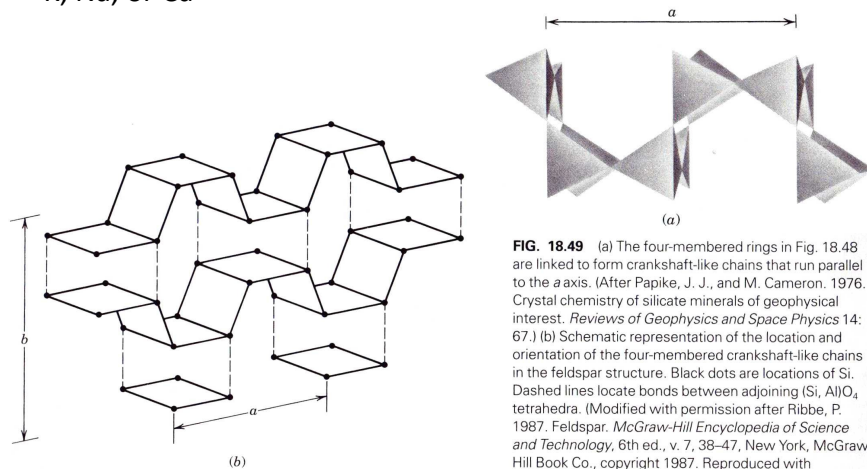
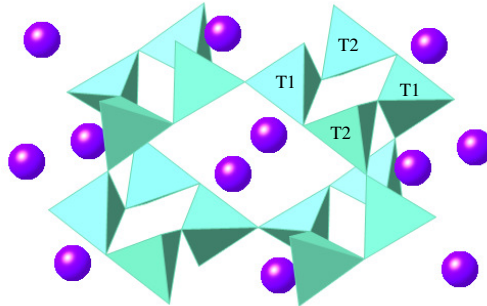


FIG. 18.49 (a) The four-membered rings in Fig. 18.48 are linked to form crankshaft-like chains that run parallel to the a axis. (After Papike, J. J., and M. Cameron, 1976. Crystal chemistry of silicate minerals of geophysical interest. *Reviews of Geophysics and Space Physics* 14: 67.) (b) Schematic representation of the location and orientation of the four-membered crankshaft-like chains in the feldspar structure. Black dots are locations of Si. Dashed lines locate bonds between adjoining (Si, Al) O_4 tetrahedra. (Modified with permission after Ribbe, P. 1987. Feldspar. *McGraw-Hill Encyclopedia of Science and Technology*, 6th ed., v. 7, 38–47, New York, McGraw-Hill Book Co., copyright 1987. Reproduced with permission of The McGraw-Hill Companies.)

- The Si and Al can be ordered, each having a distinct site
 - Example: microcline (low-temperature polymorph of $KAlSi_3O_8$)
- Or, completely disordered (random distribution)
 - Example: sanidine



Chemistry

3 main groups

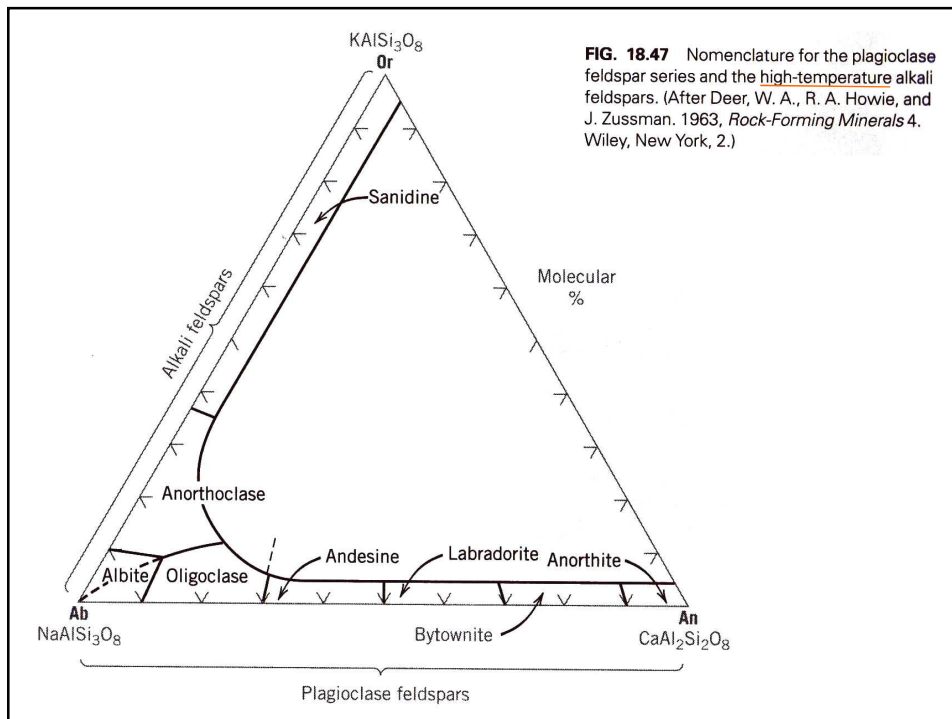
orthoclase (Or)	$KAlSi_3O_8$
albite (Ab)	$NaAlSi_3O_8$
anorthite (An)	$CaAl_2Si_2O_8$

2 solid solution series

Alkali feldspars
 $(Na,K)AlSi_3O_8$

Plagioclase feldspars
 $Ca_xNa_{1-x}Al_{1+x}Si_{3-x}O_8$
 $(x = 0 - 1)$

- Large miscibility gap
- Very little solid solution along the K-Ca edge
- Solid solution at high temperature Na-K (alkali feldspars) and Na-Ca (plagioclase)



- Very little solid solution at low-temperature (below ~ 400 °C)

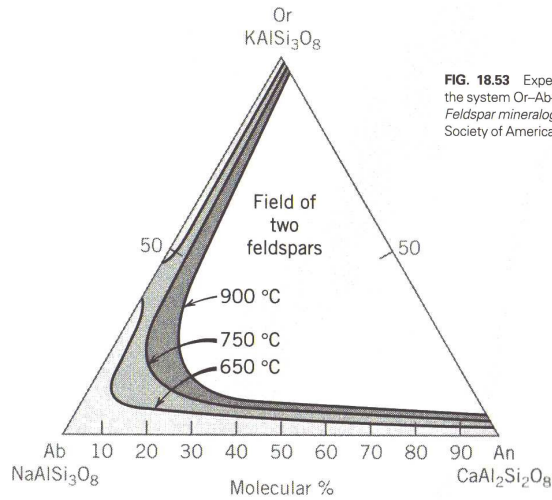


FIG. 18.53 Experimentally determined extent of solid solution in the system Or-Ab-An at $P_{H_2O} = 1$ kilobar. (After Ribbe, P. H., 1975. *Feldspar mineralogy, Reviews in Mineralogy* 2, Mineralogical Society of America, Washington, D.C., Figure R-1.)

- Many feldspars form as solid solutions, then **exsolve** (turn into 2 feldspars) at lower temperature
 - Giving rise to the **exsolution features** (e.g. perthite)

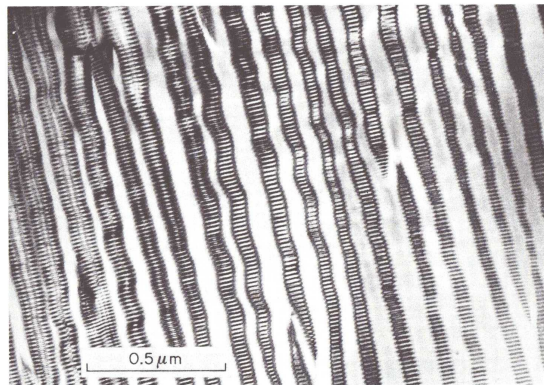


FIG. 18.52 Microstructure in an alkali feldspar of composition 57.3 weight percent Or. The Na-rich lamellae are twinned according to the albite law. This very high magnification photograph was taken with a transmission electron microscope. (From Champness, P. E., and G. W. Lorimer, 1976. Exsolution in silicates. *Electron Microscopy in Mineralogy*, H. R. Wenk, ed., Springer-Verlag, New York.)

Feldspathoids

- Typically contain more Al than the feldspars
- Important constituents of some types of silica-poor igneous rocks

Examples

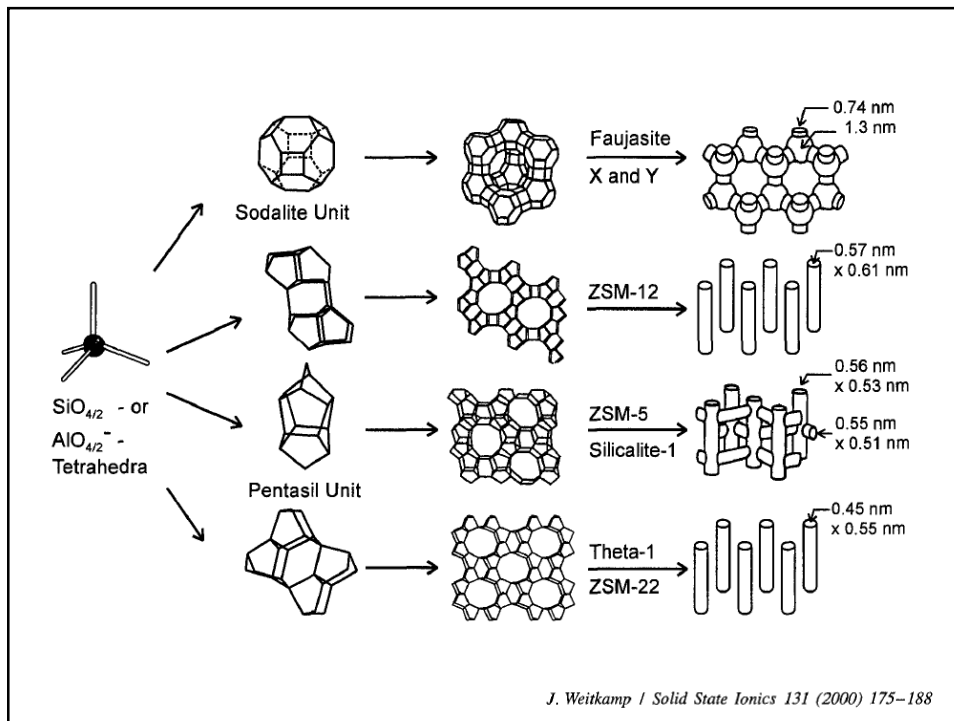
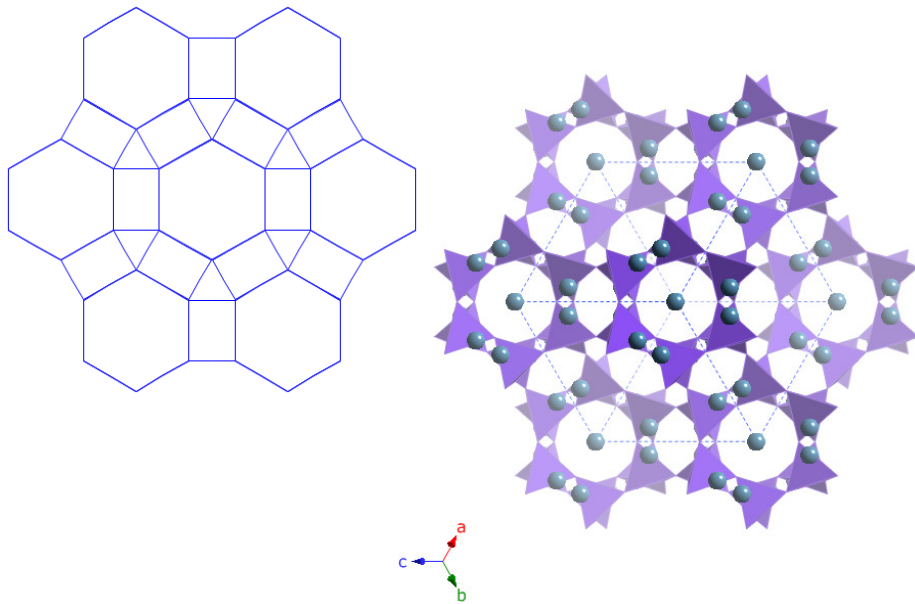
- Nepheline $(K,Na)AlSi_3O_8$: “stuffed” version of tridymite
- Leucite $KAlSi_2O_6$

Zeolites

- Greek words meaning *to boil* and *stone*
- Frameworks of AlO_4 and SiO_4
- Open frameworks, with large voids connected by channels → molecular sieve
- Hydrous: contains lots of water
- Alkali and alkaline cations – “exchangeable”



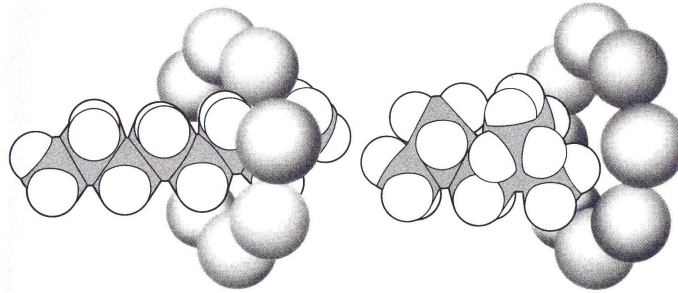
Structure of chabazite



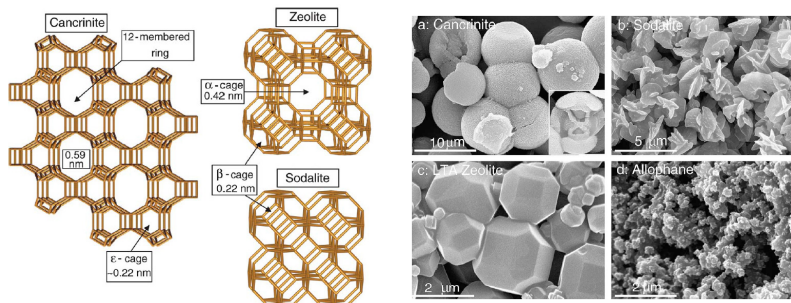
Open confined framework → molecular sieve

- Only allowing molecules with certain sizes to pass through

FIG. 18.64 Schematic illustration of how a zeolite sieve separates a straight chain hydrocarbon (e.g., octane) from a branching chain hydrocarbon (e.g., isooctane). These two organic compounds have almost identical properties and, thus, are very hard to separate by other methods. Isooctane has the higher "antiknock" rating. (From Flanigen, E. M., and F. A. Mumpton. 1977. Commercial properties of natural zeolites. *Mineralogy and Geology of Natural Zeolites, Reviews in Mineralogy* 4, Mineralogical Society America, 165–75.)



- Chemical separation
- Nuclear waste remediation
 - Removing and trapping nuclear fission products
 - Aluminum silicate framework durable and stable under radiation
 - Fukushima Daiichi nuclear disaster: trap Cs in the seawater



Cs trapped in cages!

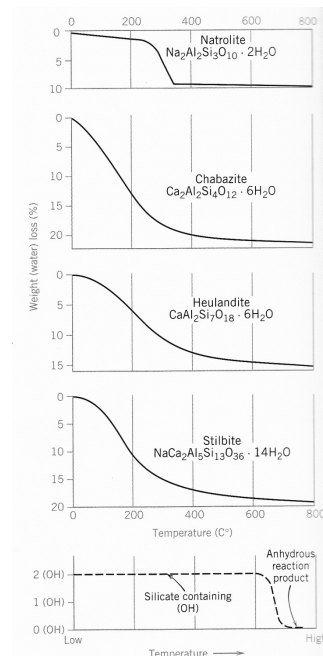
J. Mon et al. / *Microporous and Mesoporous Materials* 86 (2005) 277–286

Open confined framework → catalysis

- Used in petroleum industry for catalytic cracking
- Cracking: molecular weight reduction process by which the heavier components of crude oil are converted to lighter, more volatile materials, e.g. for gasoline
- Shape selective catalysis: confined space selects reactants, intermediate/transition products, or final products

Dehydration/rehydration

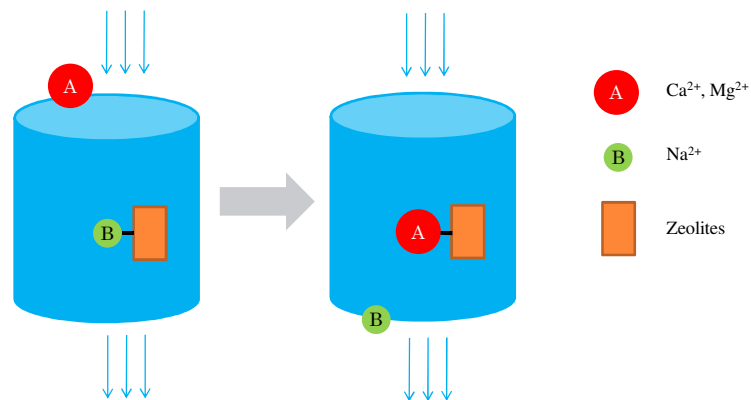
- Continuous water loss along a wide T range without structural collapse (generally up to 600 °C)
 - Similar to gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{CaSO}_4$ (~100 °C)
- Can be rehydrated
- Can still be a molecular sieve when dehydrated!
- Applications: desiccant...



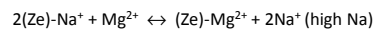
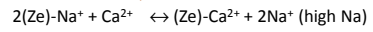
Cation exchange

- Hard water: excess amount of hardness ions (multivalent cations)
 - Dominantly Ca^{2+} and Mg^{2+}
 - Other ions: Fe^{2+} , Mn^{2+} , Sr^{2+} , Al^{3+} – not significant
- Problems:
 - Decreases the efficiency of detergents: reacts with soap preventing the formation of lather
 - Scaling of pipes, water heaters and boilers: mineral precipitation
- Typical softening methods
 - Chemical precipitation
 - Ion exchange (zeolite or resin)
 - Reverse osmosis

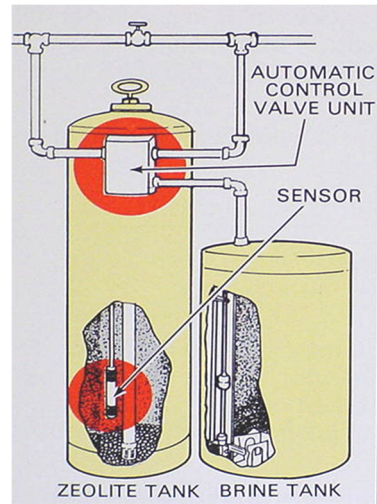
- Exchange: the displacement of one ion by another



- Regeneration with brine



Note: (Ze) represent zeolite



Next week

- Symmetry
- Reading: Klein 109-142, 169-181